Optically Active 2-Methylbutyl 3,5-Dinitrobenzoate

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A lack of agreement in the literature concerning the melting point of optically active 2-methylbutyl 3,5-dinitrobenzoate was encountered during a study of the volatile constituents of apple juice. The melting point of 2-methylbutyl 3,5-dinitrobenzoate is reported as 62°,[1] 70°[2] (both presumably from *d,l* alcohol), and 83–84°[3] (from alcohol of $[\alpha]$ +5.21°). The last value is the only one for a preparation obtained from an active alcohol of a given specific rotation. The stereoisomer available from fusel oil is *d*-2-methylbutanol, $[\alpha]^{20}D$ −5.90.[4] No data were found on the optical activity of the derivative.

An alcohol was obtained from apple juice which gave a dinitrobenzoate with a melting point of 81.5° (all melting points given here are uncorrected); its analysis was that of an amyl derivative. Mixed melting points with all inactive and racemic amyl derivatives were depressed below the melting point of either component except that with *dl*-2-methylbutyl dinitrobenzoate (m. p. 66.5°). The compound was optically active, $[\alpha]^{25}D$ +4.4°.

To determine which isomer had been obtained from apples, refined fusel oil was fractionally distilled. A fraction with $[\alpha]^{25}D$ −5.67° was obtained, equivalent to a purity of 96%. From this was prepared a 3,5-dinitrobenzoate, which melted at 83–84° and had $[\alpha]^{25}D$ +4.9°. This identified the alcohol from apples as *d*-2-methylbutanol, *i. e.*, the same as present in fusel oil.

Experimental

Dinitrobenzoate from Apple Fraction.—A distillate fraction (the full procedure appears elsewhere,[5] 0.98 g. b. p. (150 mm.) 90–100°, $n^{20}D$ 1.4104, yielded a chromatographically[6] homogeneous 3,5-dinitrobenzoate on treatment with dinitrobenzoyl chloride in the presence of pyridine. It had a m. p. of 81.5–82.5°, analyzed as an amyl derivative, and failed to depress the m. p. of only the *dl*-2-methylbutyl derivative (m. p. 66.5°), in which case the melting range was 67–79°. It was then found to have $[\alpha]^{25}D$ +4.4° (4.8% in acetone). *Anal.* Calcd. for $C_{12}H_{14}O_6N_2$: C, 51.10, H, 4.96, N, 9.93. Found: C, 51.09; H, 5.04; N, 9.99.[7]

Distillation of *d*-2-Methylbutanol from Fusel Oil.—One gallon (3.78 l.) of "isoamyl alcohol"[8] was fractionated at atmospheric pressure in a Podbielniak column operated with intermittent take-off; it yielded 200 ml. of crude *d*-2-methylbutanol, b. p. 128–129°, estimated to be 53% pure. When redistilled, this fraction yielded 65 ml. of the alcohol, 93% pure. This material, redistilled in turn, yielded a fraction, b. p. 128.5°, $n^{20}D$ 1.4105, $[\alpha]^{25}D$ −5.67°, which is 96.1% of the accepted value.[4] The 3,5-dinitrobenzoate of this fraction melted at 83–84°, and had $[\alpha]^{25}D$ +4.9° (6.4% in acetone). *Anal.* Calcd. for $C_{12}H_{14}O_6N_2$: C, 51.10; H, 4.96. Found: C, 51.00; H, 5.00. A mixed melting point with the product from apple juice was 82–84°; therefore the alcohol from apples was *d*-2-methylbutanol.

(1) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1948, p. 226.

(2) Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926).

(3) Gordon, *J. Am. Pharm. Assoc.*, **16**, 419 (1927).

(4) W. Markwald and A. McKenzie, *Ber.*, **34**, 485 (1901).

(5) White, THIS JOURNAL, in press.

(6) Chromatography was on silicic acid-rhodamine 6G by the method of White and Dryden, *Anal. Chem.*, **20**, 853 (1948).

(7) The authors are indebted to C. L. Ogg for the microanalyses.

(8) This alcohol, $[\alpha]^{25}D$ −1.06°, was kindly donated by Publicker Industries, Inc.

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